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COVER: Detail of the early Middle Horizon tapestry fragment in William J Conklin's article "Peruvian Textile Fragment from the Beginning of the Middle Horizon". Photograph by Allen C. Marceron.

DRAWINGS by: William J Conklin for "Peruvian Textile Fragment from the Beginning of the Middle Horizon"; Sally Huddles for "Symbolic Scenes in Javanese Batik"; Milton Sonday for "A Type of Mughal Sash".

PHOTOGRAPHS of Textile Museum's illustrations are by Allen C. Marceron and Osmund L. Varela. All other photographs are courtesy of American Museum of Natural History, The Brooklyn Museum, William J Conklin, Kelemen Archive, Elisabeth Z. Kelemen, Los Angeles County Museum of Art, The Metropolitan Museum of Art, and Taylor & Dull.

tion of about pH 7 can be had by the conservator. Incidentally, this same solution is reputed to minimize alkaline browning development on cottons if used as a last rinse.

Calcium hydroxide, $Ca(OH)_2$, a true alkali not mentioned earlier, is often called quicklime if used as a slurry. This alkali dissolves protein fleshy matter from bones and hides and in this way may have some application to conservation.

TABLE I

Dilution Proportions for Ammonium Hydroxide
26° Bé is approximately 28% as purchased
Household Ammonia is approximately 15% as purchased

Approximate concentration desired —Percent	Parts of 26° Bé or 28% per gallon of water		Parts of 15% per gallon of water	
0.1	½ oz.	1 gal.	1 oz.	1 gal.
0.2	1 oz.	1 gal.	2 oz.	1 gal.
0.3	1½ oz.	1 gal.	3 oz.	1 gal.
0.4	2 oz.	1 gal.	4 oz.	1 gal.
0.5	2½ oz.	1 gal.	5 oz.	1 gal.
1.0	5 oz.	1 gal.	10 oz.	1 gal.
2.0	10 oz.	1 gal.	20 oz.	1 gal.

Note: Ammonia solutions lose strength on ageing.

TABLE II

pH Values of Various Alkalies:

Name	0.1% Conc.	1% Conc.	Full Strength	
Ammonium hydroxide	8.6	9.1	11.5	26° Bé
Sodium bicarbonate	8.3	8.3		
Sodium carbonate	11.2	12.1		
Modified soda	10.3	10.3		
Neutral soap	10.0	10.0		
Sodium metasilicate	11.4			
Trisodium phosphate	11.1	11.9		

(From Applied Science for Drycleaners, G. P. Fulton, Table 4, page 56.)

NOTES

[1] Oxidized Oil Stains, *National Institute of Drycleaning Bulletin T-455*, Dec. 1969. Silver Spring, Maryland.

[2] Table 4, page 56 of *Applied Science for Drycleaners* by G. P. Fulton, National Institute of Drycleaning, Silver Spring, Maryland. 1951.

PRINCIPLES OF TEXTILE CONSERVATION SCIENCE NO. XV

THE CONTROL OF OXIDATION IN TEXTILE CONSERVATION

JAMES W. RICE

Occasionally it is necessary to employ oxidation or reduction in the treatment of textiles. Since these chemical operations are hard to control, they are considered to be last resort treatments for antique fabrics. We hope to explain the reasons therefor in this study.

Oxidation may be defined simply by saying that it is the process of adding oxygen to a compound or an element or of increasing the valence of such substances.

Reduction, on the other hand, opposes oxidation in that it takes away oxygen from a substance or decreases its valence.

As a result, these two mechanisms are used to counteract one another, although this is not exactly neutralization as in the sense of acids and alkalies.

Oxidation is a natural process because oxygen is always abundant in the air and is quite active chemically. It causes rotting, rusting, burning and other familiar chemical degradation processes that are continually in progress. Oxidation produces heat and, if confined, high temperatures, flames and even explosions. If uncontrolled, oxidation has been known to build up the temperature of a reaction to a point where spontaneous combustion occurs. Thus, one way of controlling oxidation is to cool or even refrigerate the substances involved. Fortunately, most substances have to be heated to a certain temperature before rapid ignition occurs. Nevertheless, slow oxidation of textiles happens at moderate or lower temperatures and what we call ageing or rotting results.

It may be obvious that another way to prevent or control oxidation of a substance would be to surround it with an oxygen-free shield. For example: one might store it in an atmosphere of pure helium or pure argon or it might be immersed in some liquid that does not dissolve oxygen. These controls are expensive as a rule, difficult and not always practical.

Another method of control of oxidation is by use of reducing agents. These are sometimes called antioxidants, or in dye work or spot removal, "strippers". Since they are opposite in action to oxidizers, or chemicals that furnish oxygen, we would expect reduction to absorb heat to keep it working. Reduction tends to repair some of the damage of oxidation to textile fibers or at least to prevent it for a time. This will be discussed fully in our next paper on *Principles of Textile Conservation Science No. XVI.*

OXIDIZING AGENTS AND BLEACHES

Oxidizing agents are substances that provide oxygen or bring about a change in valence towards the positive. Examples of familiar oxidizing agents when used for whitening purposes are called bleaches and are of great interest to us in textile work. A number of these will be discussed and described in detail.

In most of the examples we provide nearly all of them are suppliers of oxygen. A simple case of one in which oxygen may not be involved would be a chemical reaction indicated by the equations of formation of ferric chloride $FeCl_3$ as follows:

$$\begin{array}{llll} Fe^{\circ} & + Cl_2 \rightarrow & FeCl_2 \\ \text{valence}^{\circ} & \text{oxidizer} & \text{Fe valence 2} \end{array}$$

In this ferrous state, which is relatively unstable, the iron ion is pale green and, with continuing exposure to chlorine gas, the ferrous chloride will unite with more chlorine to form ferric chloride thus:

$$2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3$$

wherein the iron has been increased in valence to three (+++) and is now distinguished by a red color. This phenomenon will be discussed later under specific stain and spot removal problems.

BLEACHES ARE CONTROLLED OXIDIZING AGENTS

The more common bleaches are readily available in many stores and markets such as druggists, chemists shops, cleaning supply houses and groceries. We find some in compounded Trade-Marked detergents. For the conservator's work, the use of such detergents should be avoided. For our purposes one should choose a recommended product with a manufacturer's label bearing the percentage concentration. There are several main classes of these bleaches, described as follows:

THE HYPOCHLORITES

These are most commonly used especially for bleaching cotton, linen, paper and other cellulosics. Hypochlorites should not be used on wool, silk, leather, feathers or other protein textiles or similar artifacts because this fiber type has been known to be damaged by them. In fact, hypochlorites have been used to dissolve the scaly epidermis of wool fibers for producing non-felting wool for socks. In this case, the technique requires controls and expertise beyond the conservator's command.

There are several available kinds of hypochlorites: such as calcium oxychloride, CaClOCl, or bleaching powder, calcium hypochlorite, $Ca(OCl)_2$ or HTH if purchased on the market, also a powder or granules. As these granules are not very soluble, before bleaching textiles, either of them must be converted to solutions of sodium hypochlorite, NaOCl, sometimes known as Javelle water. This is done by treating a slurry of the powder with sodium carbonate solution.

Sodium hypochlorite in about five and a quarter percent concentration known as common chlorine laundry bleach is a popular product sold under numerous trade names. Probably the most widely advertised one in the Eastern United States is known as Chlorox.®

The 5.25% concentration of NaOCl is a convenient form for storage of the bleach but it should always be diluted greatly in use as it is far too rapid acting and powerful at that strength for most textile bleaching. For whitening and slow colored stain removal the concentration of NaOCl in the total bath volume should be about 0.05% to no more than 0.2%, the latter being appropriate for strong, new or unbleached cotton fabrics. Instructions for preparation of bleaching baths may be found in Table I.

In storage the NaOCl, which is an alkaline salt (because of strong alkali-weak acid composition) is relatively stable. In the presence of any acid, however, it will immediately form hypochlorous acid HOCl thus $NaOCl + H^+ \rightarrow HOCl + Na^+$. The hypochlorous acid, although relatively un-ionized, will decompose readily on contact with certain surfaces to produce hydrochloric acid and nascent oxygen thus:

$HOCl \xrightarrow[\text{with surface}]{\text{contact}} HCl + O\uparrow$. At that stage the nascent oxygen is extremely active and will react immediately with the contacting surface where possible. If an atom of nascent oxygen is in solution, it will unite with another nearby atom to form molecular oxygen, O_2, which is less active. This is inclined to bubble off and escape before contacting the surface to be bleached.

This ingenuous theory is offered to explain one of the methods of stopping the oxidation action of the hypochlorite bleaches by souring with an acid in the last rinse of a washing routine. Unless the absorbed sodium hypochlorite, NaOCl is soured or else treated with a reducing agent, as will be discussed later, the oxidizing action on the fabric will continue for a relatively long time after and fiber strength will be lessened.

Up to this point we have dealt with the use of hypochlorites in textile conservation only. But as a matter of interest, they are employed in paper manufacture and bleaching and in great quantities for disinfection of water for drinking purposes.

Sodium chlorite, $NaClO_2$, a chemical relative of hypochlorites, has been mentioned in literature as an efficient whitening agent for textiles and paper.[1 and 2] Unfortunately, unless thoroughly rinsed out afterwards, sponteneous combustion may occur in the fabrics when this agent is allowed to dry on them and reacts with oxygen from the air to form sodium chlorate, $NaClO_3$, a very flammable and dangerous product.

THE PEROXIDES

Earlier, we have cautioned the reader to avoid using chlorine bleaches on protein fibers. For this fiber class we are fortunate in being able to bleach with the peroxide group of chemicals and obtain satisfactory results with less oxidation damage. The most widely used members of this group are hydrogen peroxide, H_2O_2, and sodium perborate $NaBO_2$. $3HOH.H_2O_2$, a complex crystallization form of sodium metaborate $NaBO_2$ which, on dissolving in water, yields hydrogen peroxide, H_2O_2.

BLEACHING BY PEROXIDE

This chemical is a popular bleach and readily available in several strengths. The most widely used of these is a three percent concentration (3%) formerly known as "ten volume" peroxide. This is relatively safe because it is unlikely to produce spontaneous combustion in an accidental contact with flammable substances. It is also considered to be an antiseptic and, when diluted, a hair bleach. For these reasons, we favor it for certain oxidation jobs in the textile conservation field.

For those who need hydrogen peroxide in large quantities or more concentrated form, it is available in thirty percent (30%) or one hundred volume strength. This is far too concentrated for our use unless greatly diluted. It can be purchased in gallon-sized bottles from cleaners and drug supply houses but it must be handled and stored with great care because of its flammability hazards. Some large volume cleaners and other users purchase this strength for economy reasons.

Hydrogen peroxide, H_2O_2, is a very weak acid and is also unstable. Its contact with surfaces, especially those of the textile fibers, has a catalytic effect which causes it to decompose. Thus

$$H_2O_2 \xrightarrow[\text{fiber surface}]{\text{on a}} H_2O + O\uparrow \text{ (nascent oxygen) the}$$

active state of oxygen encountered before, and which oxidizes or bleaches the surface immediately.

This oxygen yield can be greatly accelerated by heating, by exposeure to light, by contact with hydroxyl ions (^-OH) and by various metals, especially iron.

From this information we may deduce precepts for storing and controlling our hydrogen peroxide in use. First, we keep it in a cool dark storage closet. The containers should be of colored, preferably brown, glass to provide protection from light and also the least surface of contact. To make sure that no hydroxyl ions are present, the solution should be slightly acidic, at least until it is actually being used.

For bleaching, the bath should be prepared in a glass, glazed enamel ware, stoneware or similar type vessel of suitable dimensions. Metal containers, especially iron, should be avoided. However, some types of plastic linings may be acceptable.

Dilution, Table II, will provide suggestions as to dosage for various bath volumes. In practice, it is wise to start off with a low concentration and moderately low temperature, perhaps 70° Fahrenheit. Warm the water first, immerse the fabric into water of the same temperature, add the measured peroxide (3% grade) to the bath and enter the saturated fabric. Stir with a glass or plastic rod until the goods are covered with the diluted bleach solution. Keep the fabric completely immersed and observe for 10 to 20 minutes for effect. If decoloration is satisfactory, remove and rinse several times in warm water 100-120° F.

This step is recommended for cotton or other cellulosic fibers to get rid of any adsorbed peroxide. For wool and proteins, the control of continuing oxidation may be done by adding an antioxidant such as sodium bisulfite, $NaHSO_3$, at about 1/10 percent of the bath concentration. This is not advisable for control of oxidation on cellulose because it is adsorbed on the fiber and on further oxidation becomes sulfuric acid which subsequently destroys it.

In case the decoloration has not responded, the above procedure may be repeated at a little greater concentration and if needs be at a higher temperature.

Mildew stains may be overcome with treatment by brushing with ½% hydrogen peroxide followed by exposure to sunlight in drying. In this case, the light activates the decomposition of the peroxide in situ.

As a bit of curious information—hydrogen peroxide may be used to identify dried blood spots. If a dark brown unknown spot is treated with a drop of 3% hydrogen peroxide, and foams vigorously, we believe that it is caused by iron and so we suspect blood or rust.

BLEACHING WITH SODIUM PERBORATE

Sodium perborate, $NaBO_2 \cdot 3H_2O \cdot H_2O_2$, is a modern laundry bleach quite widely used and recommended for home laundry purposes especially where white woolen goods and delicate cottons are involved. It is readily available at most supermarkets, drugstores, and cleaners' suppliers under its generic name or under various trade names such as Lestaire ® (See Note 3). As purchased, it is a granular powder. This happens to be one of its virtues. In the Lestaire mentioned above it is conveniently put out in one ounce packages.

Theoretically, sodium perborate powder is limited as to solubility to approximately two ounces of the crystals to a gallon of water. When dissolved to

the limit of solubility, which is about 1.5 percent concentration in terms of the actual weights, the active hydrogen peroxide concentration is no more than 0.33 percent. Because of this peculiar solubility effect, our perborate has a built in safety feature and it is not likely to be too concentrated for safe bleaching.

For bath bleaching of relatively unoxidized goods, the proportions of two ounces of the sodium perborate powder to a gallon of room temperature water, about 70°F., is a common proportion. The time of exposure may be from one to twenty-four hours, depending on how stubborn the stain is. This time of bleaching may be shortened by heating the bath, but it must never go over 140°F. because at that temperature the sodium perborate decomposes spontaneously into molecular oxygen which bubbles off. This is another safety feature which however is not quite so trustworthy as the solubility effect.

For bleaching very old white cotton goods, the concentration proportions may be reduced to one ounce of the perborate per gallon of water. This was done by the author in one case of bleaching an old white cotton bedspread which was spotted with numerous brown rings and large dark areas. These were presumed to be water stains of long ago. The bleach bath concentration chosen for this job was one ounce of perborate per gallon of bath. The weight of material was two pounds and the bath volume eight gallons. The bath temperature at the start was 120° F. After four hours of soaking it had dropped to 65° F. The spread was removed from the bath and allowed to drain. As a precaution against residual alkalinity which sometimes fosters brown staining after drying cottons, the spread was immersed in an eight-gallon bath of 100° F. water containing seven ounces of borax and five ounces of boric acid. This mixture forms a buffer solution of very nearly pH7. When dried on the fabric, it has flame retarding properties and also the boron atoms are said to inhibit future brown discolor.[4 and 5]

SPOT BLEACHING

The several favorable properties of sodium perborate also permit its use for spot bleaching. This is an excellent technique, especially where sophisticated spotting equipment such as a steam-air-vacuum spotting board (Figure 1) is available and conservation personnel is trained and experienced in its use.

The procedure for this is essentially as follows:

1. The fabric is draped with the spot over the grid section of the spotting board.

2. The spot is then wet out with water condensed from the steam jet held at a distance from the fabric.

3. Sodium perborate crystals are spread over the spot with a bone or plastic spatula.

4. The crystals are moistened by condensed steam as before.

5. To activate the sodium perborate, the steam nozzle is brought carefully closer to the moistened crystals. The bleaching takes place at this time when it may be noted that the perborate begins to foam. This indicates that molecular oxygen with some active nascent oxygen is in contact with the stain substance.

6. By careful watching, the bleach action can be observed and, when a satisfactory color change is attained, then the spent perborate may be flushed through the fabric and grid by combined action of the cooled condensate jet and the vacuum collector.

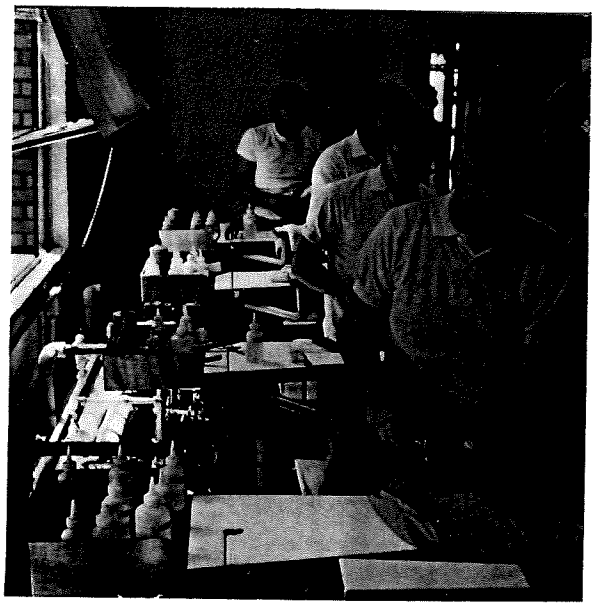

Fig. 1 *Steam-air-vacuum spotting board, Courtesy of National Institute of Dry Cleaning.*

OTHER OXIDIZERS OCCASIONALLY ENCOUNTERED IN CONNECTION WITH TEXTILE OR PAPER CONSERVATION

Oxidizing agents that are much less commonly mentioned in conservation literature are discussed briefly in the following paragraphs to complete our story.

Potassium permanganate, $KMnO_4$, a very powerful bleach, comes as crystals which dissolve to form a purple liquid. In turn, this reacts with fiber surfaces to leave a brown stain, manganese dioxide, MnO_2, behind. If this stain is treated with a reducing agent or by a reducing process and rinsed thoroughly, the stained area appears white. The brown insoluble manganic ion (Mn^{++}_{++}) in this case is converted to a manganous ion (Mn^{++}) which is pale colored and soluble. This bleach is rated as a very drastic agent and is not recommended for most conservation work.

Sodium peroxide, NaO_2, which on dissolving in water produces hydrogen peroxide, H_2O_2, and sodium hydroxide, NaOH, is a powerful and rapid bleaching agent. It is difficult to control and will leave behind the strong caustic sodium hydroxide which, unless neutralized quickly, will damage protein fibers and will affect cellulosics by causing browning. It is not recommended for use in most conservation problems.

Ozone, O_3, is the third form of oxygen that may be encountered in our work. This may be produced by sparking discharges from electrical equipment and by lightening and, as a gas, may be found temporarily in the atmosphere after thunder storms or in the vicinity of electric motors and generators. Another source is in oxygen exposed to ultra violet light as in bright sunlight. This is expected to explain the manner in which cottons and especially linens are bleached by exposure to dewey grass and bright sun. The ultra violet light produces ozone which when in contact with the moist fabric surface immediately decomposes again to give nascent oxygen which does the bleaching. Thus

$$3\ O_2 \xrightarrow[\text{spark of ultra violet ray}]{\text{influenced by electric}} \text{produces } 2\ O_3 \text{ ozone}$$

(a toxic gas). However, when it contacts a wet surface, such as damp fibers, the reaction reverses and $O_3 \rightarrow O_2 + O$ (nascent oxygen). This is a momentary existence for the latter and it will unite immediately, preferably, with any nearby reducing substance or else with another atom of nascent oxygen to form the less active molecular oxygen. Manufactured ozone is not easily handled with equipment available to the conservator and is more of a nuisance than a usable bleaching agent. It might account, however, for excessive oxidation in some circumstances. One of the uses of ozone is for destroying odors in fabrics.[6]

Potassium monopersulfate, KHS_2O_6, a bleaching agent marketed under the trade name Oxone® (Note 7), is a powder available at some supermarkets. According to the labels of a product called Beads O Bleach® (Note 8), which contains Oxone® it is recommended for bleaching nylon and other synthetic fibers that have been treated with resins for crease and stain resistance. Such resins if bleached by hypochlorites develop objectionable odors which do not occur when the potassium monopersulfate is used. Recommended concentrations would be two tablespoonsful of powder per gallon of hot water. Time of bleaching is about 20 to 30 minutes. For stubborn stains double the dosage but not the time of bleaching.

Chloramine-T, 1 CH_3-C_6H_4-4-SO_2NClNa, an organic bleach which is of limited solubility in water, is an interesting bleach used for removing stains from paper because the chlorine atom does the oxidizing without producing oxycellulose, a product which denotes molecular weakening in cellulose after bleaching with the hypochlorites.[9] A near relative dichloramine-T, 1 CH_3-C_6H_4-4-SO_2NCl_2 has been suggested as a possible bleach for use in nonaqueous solvents such as some special drycleaning media. In this case, the oxidation must be done in a fume closet as the vapors of the better solvents are quite toxic.

TABLE I

Dilution Tables for 5.25% sodium hypochlorite laundry bleach for a one gallon bath:

% of bleach	0.5	0.4	0.3	0.2	0.1
Ounces of 5.25% bleach	12	9.6	7.2	4.8	2.4

To be used for cotton, linen, or paper only. Recommended bath temperature 100-120° F. Bath volume about one gallon to 6 ounces of fabric or yarn.

TABLE II

Dilution Tables for 3% hydrogen peroxide bleach for a one gallon bath:

% of bleach	0.5	0.4	0.3	0.2	0.1
Ounces of 3% peroxide	21.5	17.2	12.9	8.6	4.3

May be used for wool and other protein fibers and also for cotton, paper, and other cellulosics. Recomended bath temperatures 100-120°F. Bath volume one gallon for 6 ounces of fabric or yarn.

NOTES

[1] *Applied Science for Drycleaners* by G. P. Fulton. Page 227. National Institute of Drycleaning, 1951.

[2] *The Conservation of Antiquities and Works of Art* by H. J. Plenderleith. Page 60. Oxford University Press, London, 1956.

[3] Lestaire® is a trade-marked product sold by Standard Household Products Corporation, Holyoke, Massachusetts.

[4] *National Institute of Drycleaning Technical Bulletin T-335*. November 1954. Effect of boron ion on brown stain development.

[5] *Wetcleaning* by N. J. Berg. Page 220. National Association of Cleaners and Dyers, 1945.

[6] *Applied Science for Drycleaners* by G. P. Fulton. Page 229. National Institute of Drycleaning, 1951.

[7] Oxone® is a registered trade-marked product manufactured by the E. I. du Pont de Nemours Co. of Wilmington, Delaware.

[8] "Beads-O-Bleach" is a trade-marked product marketed by Purex Corporation of Lakewood, California.

[9] *The Conservation of Antiquities and Works of Art* by H. J. Plenderleith. Page 77. 5 Ed. Oxford University Press, London, 1966.